THE STRUCTURE AND PROPERTIES OF SOME METALLIC DERIVATIVES OF DYES

I. AZO DYES
II. SUBSTITUTED 8-HYDROXYQUINOLINES

BY

JENNIE CHING-I LIU

B.S., St. John's University, 1946
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Part I. Azo Dyes

Previous investigation has shown definitely that lake formation with metals increases the stability of azo dyes, particularly toward light and washing. The stability of the lake, as well as that of the dye itself, is enhanced by inner coordination of the metal with the azo nitrogen; such forms arise only when the metal is affixed by covalent linkage to substituents, e.g. OH, COOH, NH_2, etc. ortho to the azo linkage. Consequently the presence of two constituents of this kind in the o,o′ positions further increases the stability of the lake which assumes a fused ring formation. Meta or para substituents have no such effect.

Generally, the metal combines with the dye molecule by replacing the hydrogen atom from the hydroxy or carboxy group and accepting an electron pair donated by the oxygen and the azo nitrogen atoms. The chelate ring thus formed consists of five or six members which is in the most stable form. Due to the fact that nitrogen in the pyridine ring possesses an unshared electron pair, it would be expected that α-pyridyl azo compounds would donate an additional covalent bond to the metal through the pyridyl nitrogen. Hence, an investigation of some lakes of α-pyridyl derivatives of β-naphthol and resorcinol was undertaken.

With α-pyridyl azo-β-naphthol, the divalent metallic lakes, like those of copper and nickel, were found to contain one azo residue to one metallic atom, the second valency of the metal being balanced by an acidic ion. In the case of trivalent metallic lakes, like those of chromium, cobalt and iron, dye:metal complexes in the ratio 2:1, were found. In these also, the complex is a monovalent, positive ion.

The presence of an additional hydroxy group para to the azo linkage as in the case of α-pyridyl azo resorcinol gives

water soluble lakes of similar type with an additional primary valence of the metal satisfied by the replacement of the hydrogen ion from the dye molecule.

A study of some lakes of α-(o-carboxy-azobenzene)-o′-chloroacetoacetanilide and of 2′-carboxybenzene 4-azo-1-phenyl-3-methyl-pyrazol-5-one has been made to extend further the knowledge of the azo lakes. After enolization these two o-carboxy-azo-o′-ketonyl dyes are structually similar to the o-carboxy-azo-o′-hydroxy compounds.

Spectrophotometric determination and magnetic measurements have been used in some cases to study further the structure and the properties of the lakes.

BIBLIOGRAPHY

1. Drew, H.D.K. and Landquist,J.K., J. Chem. Soc. 292 (1938)
2. Drew, H.D.K. and Fairbairn,R.E., J. Chem. Soc. 823 (1939)
3. Drew, H.D.K. and Beech,W.F., J. Chem. Soc. 603 (1940)
4. Drew, H.D.K. and Dunton,F.G., J. Chem. Soc. 1064 (1940)
5. Callis, C.F., M.S. Thesis, Univ. of Ill. (1946)
6. Callis, C.F., Ph.D. Thesis, Univ. of Ill. (1948)

Part II. Substituted 8-Hydroxyquinolines

Although methods involving the use of 8-hydroxyquinoline (or oxine) as a quantitative precipitant have been extensively investigated and widely used, little structural information about the complexes so formed can be obtained. Since polar groups, e.g. OH, COOH or SO_3H para to the point of coupling with the aromatic nucleus are completely independent of the coordination sphere and act merely as the solubility promoting vehicles, an investigation of the structural and stereochemical properties of the substituted 8-hydroquinolines in comparison with the parent substance was undertaken. The

particular derivative chosen for this work was 8-hydroxyquinoline-5-sulfonic acid.

Cadmium and zinc derivatives of oxine-5-sulfonic acid were found to be fluorescent in aqueous medium as well as cadmium and zinc oxinates in chloroform. But copper and nickel derivatives of the same dye were found to be not fluorescent at all.

Spectrophotometric study indicated that a 2:1 dye:nickel complex is formed in aqueous solution.

Structural study of copper derivative of oxine-5-sulfonic acid showed that its composition varies somewhat with the amount of reagents present and its color varies with the amount of water it contains.

A conclusive proof that the zinc derivative of oxine-5-sulfonic acid has a tetrahedral configuration would lie in its resolution into optically active isomers. Strychnine was found to be a satisfactory resolving agent. From the rotation data obtained, it is evident that at least partial resolution was accomplished.

BIBLIOGRAPHY

1. Berg, R., Das Chemische Analyse, Vol. XXXIV, Das O-oxychinolin "Oxin", F. Enke, Stuttgart (1935)

2. Welcher, F.J., Organic Analytical Reagent, Vol. I, D. Van Nostrand Co., N.Y. (1947)

VITA

The author was born on May 16, 1925, in Soochow, China. She attended Ying Hwa Primary School in Soochow. When Sino-Japanese War broke out in August, 1937, she went to Shanghai, China, and attended Besant High School for Girls. She entered St. John's University, Shanghai, in June, 1942, and received the degree of Bachelor of Science in Chemistry, with honors, from that institution in January, 1946. In June of that year, she was awarded the "Best in Science" prize for acheiving the highest scholastic average in the school of Science in the academic year 1945-46.

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